CCSF PHYC 4D Lecture Notes

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Chapter 5
The Schrodinger Equation

Wave function normalization

- Recall that a simple particle confined to one dimension can be expressed as a probability wave by giving its wave function $\psi(x,t)$ as a function of position and time. The probability of finding the particle in a small interval $[x, x+dx]$ at time t is given by

$$P(x,t)\,dx = |\psi(x,t)|^2\,dx = \psi^*(x,t)\psi(x,t)\,dx$$

  z^* denotes the complex conjugate of z.

- The probability that the particle exists in some (non-small) interval $[x_1, x_2]$ can be computed by integration

$$P([x_1,x_2]) = \int_{x_1}^{x_2} P(x,t)\,dx = \int_{x_1}^{x_2} |\psi(x,t)|^2\,dx$$

- Since the particle must exist somewhere (with probability 1), it follows that

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2\,dx = 1$$

  A wave function that satisfies this condition is said to be *normalized*. Wave functions should be normalized at every instant in time.

- Normalizing a wave function is a matter of imposing the normalization condition above and solving for an overall factor. As an example, consider a Gaussian wave packet centered at x_0 and width σ_x, given in general by

$$\psi(x) = C\exp\left(-\frac{(x-x_0)^2}{4\sigma_x^2}\right)e^{ik_0x}$$

  The normalization condition leads to

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} |\psi(x)|^2\,dx = \int_{-\infty}^{\infty} |C|^2\exp\left(-\frac{(x-x_0)^2}{2\sigma_x^2}\right)\,dx \\ &= |C|^2\sqrt{\frac{\pi}{1/(2\sigma_x^2)}} = |C|^2\sigma_x\sqrt{2\pi} \end{aligned}$$

  This implies

$$|C| = (2\pi)^{-1/4}\sigma_x^{-1/2}$$

The complete normalized wave function can be written

$$\psi(x) = (2\pi)^{-1/4}\sigma_x^{-1/2}\exp\left(-\frac{(x-x_0)^2}{4\sigma_x^2}\right)e^{ik_0x}$$

possibly multiplied by an overall phase factor of the form $e^{i\phi}$.

- Normalizing localized wave functions, such as the Gaussian wave packet, can easily be done, at least in principle. Normalizing unlocalized wave functions cannot be done since the integrals diverge. For example, consider the wave function of a particle with definite momentum $p = \hbar k$.

  $$\psi(x) = Ae^{ikx}$$

  The probability density is constant

  $$P(x)\,dx = |\psi(x)|^2\,dx = |A|^2\,dx$$

  If we attempt to normalize $\psi(x)$, we run into trouble immediately

  $$1 = \int_{-\infty}^{\infty}|A|^2\,dx = |A|^2(\infty)$$

- The problem is that an unbounded wave function such as the single-k wave spreads its probability over an infinite region. If that were truly possible, the probability of finding such a particle in any finite subregion would have to be zero.

- One solution is to recognize the single-k wave function as an idealization, as a limit of a wave packet formed from a very narrow band of k values (consider $A(k)$ vs. k as a spike centered at k_0). Such a wave packet would be spread over a very large, but finite, region in x (such as the Gaussian above). As $\sigma_k \to 0$, $\sigma_x \to \infty$ (by the uncertainty principle) and the normalization constant would go to zero. But for any *finite* value of σ_k, the normalization procedure would lead to a valid wave function.

- Another solution is to reinterpret the wave function, not as a probability amplitude for a *single* particle, but as some sort of density amplitude of a whole *stream* of particles. Consider an infinite line of particles with a uniform particle density ρ, all moving with a single value of momentum $p = \hbar k$. Such a particle stream can be described by a wave function

  $$\psi(x) = Ae^{ikx}$$

defined so that $|\psi(x)|^2\,dx$ gives the expected number of particles located in the range $[x, x+dx]$. Normalizing the wave function this way yields

$$\rho\,dx = |\psi(x)|^2\,dx = |A|^2\,dx$$

which implies $|A| = \sqrt{\rho}$.

- In a more sophisticated treatment of quantum mechanics, one is likely to see the entire family of single-k wave functions $\psi_k(x) = A_k e^{ikx}$ normalized using *delta-function normalization*.

$$\int_{-\infty}^{\infty} \psi_{k_1}^*(x)\psi_{k_2}(x)\,dx = \delta(k_1 - k_2)$$

The delta-function $\delta(x)$ is defined (as a limit of functions) such that $\delta(x) = 0$ if $x \neq 0$ and $\int_{-\infty}^{\infty} \delta(x)\,dx = 1$ (this implies $\delta(0) = \infty$). The delta-function normalization condition leads to $A_k = 1/\sqrt{2\pi}$ and thus

$$\psi_k(x) = \frac{1}{\sqrt{2\pi}} e^{ikx}$$

- Delta-function normalization is not adopted so much for interpretive reasons (single-k wave functions are not regarded as valid states themselves, but as the limit of a series of wave packets, as discussed above), but to provide a properly normalized "basis" in which all valid wave functions can be expressed. Indeed, the Fourier transform can be expressed in terms of these "normalized" functions

$$\psi(x) = \int_{-\infty}^{\infty} A(k) \frac{e^{ikx}}{\sqrt{2\pi}}\,dk$$

$$A(k) = \int_{-\infty}^{\infty} \psi(x) \frac{e^{-ikx}}{\sqrt{2\pi}}\,dx$$

The result is more symmetric — the factor of 2π is now shared between the Fourier transform equation and its inverse. We will not adopt this convention, but you will see it in more advanced quantum mechanics textbooks, and it does offer theoretical advantages.

Computing expectation values

- When a certain quantity q can take on values q_1, q_2, ..., with probabilities p_1, p_2, ..., the *expectation value* of q is given by

$$\langle q \rangle = \sum_i q_i p_i$$

- $|\psi(x)|^2\,dx$ gives the probability of finding the particle in the interval $[x, x+dx]$. This information can be used to calculate expectation values of any function $f(x)$, as follows:

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x)(P(x)\,dx) = \int_{-\infty}^{\infty} f(x)|\psi(x)|^2\,dx = \int_{-\infty}^{\infty} \psi^*(x) f(x) \psi(x)\,dx$$

  One must use a *normalized* wave function for this to work.

- The uncertainty of x can be calculated in terms of these expectation values:

$$\delta x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

- Consider the Gaussian wave packet:

$$\psi(x) = (2\pi)^{-1/4} \sigma_x^{-1/2} \exp\left(-\frac{(x-x_0)^2}{4\sigma_x^2} \right) e^{ik_0 x}$$

  Then

$$\begin{aligned} \langle x - x_0 \rangle &= \int_{-\infty}^{\infty} (x - x_0)|\psi(x)|^2\,dx \\ &= \frac{1}{\sigma_x \sqrt{2\pi}} \int_{-\infty}^{\infty} (x - x_0) \exp\left(-\frac{(x-x_0)^2}{2\sigma_x^2} \right) dx \\ &= 0 \end{aligned}$$

  since the integrand is an odd function of $x - x_0$. This implies that $\langle x \rangle = x_0$. Likewise,

$$\begin{aligned} \langle (x - x_0)^2 \rangle &= \int_{-\infty}^{\infty} (x - x_0)^2 |\psi(x)|^2\,dx \\ &= \frac{1}{\sigma_x \sqrt{2\pi}} \int_{-\infty}^{\infty} (x - x_0)^2 \exp\left(-\frac{(x-x_0)^2}{2\sigma_x^2} \right) dx \\ &= \frac{1}{\sigma_x \sqrt{2\pi}} \int_{-\infty}^{\infty} (2\sigma_x^2) u^2 e^{-u^2} (\sigma_x \sqrt{2}\,du) \qquad u = \frac{x - x_0}{\sigma_x \sqrt{2}} \\ &= \frac{2\sigma_x^2}{\sqrt{\pi}} \int_{-\infty}^{\infty} u^2 e^{-u^2}\,du \end{aligned}$$

$$= \frac{2\sigma_x^2}{\sqrt{\pi}} \frac{\sqrt{\pi}}{2} \qquad \text{(integrate by parts)}$$
$$= \sigma_x^2$$

which implies that $\delta x = \sqrt{\langle (x - x_0)^2 \rangle} = \sigma_x$.

Wave number and momentum distributions

- A single-k wave function given by

  $$\psi(x) = Ae^{ikx}$$

  represents a particle with a definite momentum $p = \hbar k$. If several waves with different k values are combined, the momentum can take on several different possible values of momentum with probabilities that depend on the relative amplitudes of the waves. For example,

  $$\psi(x) = \sum_{n=1}^{N} A_n e^{ik_n x}$$

  can take on any of the N values of momentum $\hbar k_1$, $\hbar k_2$, ..., $\hbar k_N$. The probability that the momentum is $\hbar k_n$ (as opposed to some other value) is proportional to $|A_n|^2$. Note that no finite sum of waves can be properly normalized since $\psi(x)$ will not be a *localized* wave packet.

- If we consider a continuous superposition

  $$\psi(x) = \int_{-\infty}^{\infty} A(k) e^{ikx}\, dk$$

  then the distribution of momentum values is determined by the amplitude function $A(k)$. The probability that the wave number is in the interval $[k, k+dk]$ (placing the momentum in the interval $[\hbar k, \hbar(k+dk)]$) is proportional to $|A(k)|^2\, dk$.

- To get the proper proportionality constant (it is not 1, unfortunately), we need to determine the normalization condition for $A(k)$. This can be obtained from the normalization condition for $\psi(x)$.

  $$\int_{-\infty}^{\infty} |A(k)|^2\, dk \;=\; \int_{-\infty}^{\infty} dk\, A^*(k) A(k)$$

$$
\begin{aligned}
&= \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, \left(\int_{-\infty}^{\infty} dx\, \psi^*(x)(e^{-ikx})^*\right) A(k) \\
&= \frac{1}{2\pi}\int_{-\infty}^{\infty} dx\, \psi(x)^* \int_{-\infty}^{\infty} dk\, A(k) e^{ikx} \\
&= \frac{1}{2\pi}\int_{-\infty}^{\infty} dx\, \psi(x)^* \psi(x) \\
&= \frac{1}{2\pi}
\end{aligned}
$$

It follows that

$$\int_{-\infty}^{\infty} 2\pi |A(k)|^2\, dk = 1$$

and so

$$P(k)\, dk = 2\pi |A(k)|^2\, dk$$

represents the probability that the wave number lies in the interval $[k, k+dk]$.

- Applying the normalization condition to the Gaussian

$$A(k) = A \exp\left(-\frac{(k-k_0)^2}{4\sigma_k^2}\right) e^{-ikx_0}$$

yields (same calculation as before, except for an extra 2π)

$$|A| = (2\pi)^{-3/4}\sigma_k^{-1/2}$$

When we did the wave packet calculation in Chapter 4, we found that $C = A\sigma_k\sqrt{4\pi}$, and so

$$
\begin{aligned}
|C| &= |A|\sigma_k\sqrt{4\pi} = (2\pi)^{-3/4}\sigma_k^{-1/2}\sigma_k\sqrt{4\pi} \\
&= (2\pi)^{-1/4}(2\sigma_k)^{1/2} = (2\pi)^{-1/4}\sigma_x^{-1/2}
\end{aligned}
$$

The last equality is from the uncertainty relation $\sigma_k\sigma_x = \frac{1}{2}$. Evidently, a properly normalized amplitude function will automatically lead to a properly normalized wave function.

- Expectation values of any function of wave number $f(k)$ can be obtained from the amplitude function as follows:

$$\langle f(k)\rangle = \int_{-\infty}^{\infty} f(k) 2\pi |A(k)|^2\, dk = \int_{-\infty}^{\infty} 2\pi A(k)^* f(k) A(k)\, dk$$

Functions of momentum $f(p)$ can be written as functions of wave number $f(\hbar k)$ and evaluated accordingly. For example, the expected value and uncertainty of momentum for a Gaussian wave packet can be computed from the amplitude function in much the same way that we computed the expected value and uncertainty of position from the wave function. The result is

$$\langle p \rangle = \hbar k_0 \qquad \delta p = \sqrt{\langle (p - \langle p \rangle)^2 \rangle} = \hbar \sigma_k$$

The uncertainty principle follows:

$$(\delta x)(\delta p) = \sigma_x \hbar \sigma_k = \tfrac{1}{2}\hbar$$

- Expectation values of momentum (and any functions thereof) can also be computed directly from the wave function $\psi(x)$ with the help of the *momentum operator*

$$\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$$

If we apply this operator to a single momentum state

$$\psi(x) = Ae^{ikx}$$

we get

$$\hat{p}\psi(x) = \frac{\hbar}{i}\frac{d}{dx}(Ae^{ikx}) = \frac{\hbar}{i}ikAe^{ikx} = \hbar k\psi(x)$$

Expectation values can be computed as follows:

$$\begin{aligned}
\int_{-\infty}^{\infty} \psi(x)^* \hat{p}\psi(x)\, dx &= \int_{-\infty}^{\infty} dx\, \psi(x)^* \hat{p} \int_{-\infty}^{\infty} dk\, A(k)e^{ikx} \\
&= \int_{-\infty}^{\infty} dx\, \psi(x)^* \int_{-\infty}^{\infty} dk\, \hbar k A(k)e^{ikx} \\
&= \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dx\, (\psi(x)^*(e^{-ikx})^*)\hbar k A(k) \\
&= \int_{-\infty}^{\infty} dk\, 2\pi A(k)^* \hbar k A(k) \\
&= \langle p \rangle
\end{aligned}$$

The same thing happens if we plug in any function of momentum

$$\langle f(p) \rangle = \int_{-\infty}^{\infty} \psi(x)^* f(\hat{p})\psi(x)\, dx$$

- More advanced treatments of quantum mechanics make heavy use of operators. Evidently, each possible observable quantity q has an associated operator $\hat{q}$ which represents that quantity. Any wave function ψ_q that represents a definite (100% likely) value of q will be an *eigenstate* of that operator:

$$\hat{q}\psi_q = q\psi_q$$

Expectation values of $f(q)$ can be obtained from ψ with the help of the operator:

$$\langle f(q)\rangle = \int_{-\infty}^{\infty} \psi(x)^* f(\hat{q})\psi(x)\, dx$$

We will not be persuing operators very deeply, but they will come up when we introduce the Schrodinger Equation (the Hamiltonian operator represents energy) and also when we study the hydrogen atom (angular momentum will show up).

The Schrodinger Equation

- The wave function provides a complete kinematic description of the particle. Information about both its position and momentum is present in the wave function $\psi(x,t)$ at any given time t. One question we might have is that if we have this complete information at some initial time, say $t = 0$, can we calculate the subsequent behavior of this particle? Can we determine $\psi(x,t)$ for all $t \geq 0$ once we know $\psi(x,0)$? As we will presently learn, the answer is yes, provided that we have complete information about the particle's interactions with its environment.

- It pays to recall how this is done in classical mechanics. In classical mechanics, the complete kinematic description of a particle is its position as a function of time $x(t)$. If we know the particle's position and velocity (or momentum) at $t = 0$, we can compute its motion for subsequent time by applying *Newton's Second Law*

$$\vec{F}_{\text{net}} = \frac{d\vec{p}}{dt} = m\vec{a}$$

The net force $\vec{F}_{\text{net}}$ can be computed once we have a complete knowledge of the particle's interactions, and the *force laws* that govern those interactions. Recall that Newton's Second Law is incomplete without those

force laws, but also that Newton's Second Law by itself has physical content: Newton promises that the force laws will be *simple*. This law sets the program for studying nature. Recall also that when we studied relativity, we actually adjusted Newton's Second Law by changing the definition of momentum, in order to retain this simplicity.

- In quantum mechanics, the position and momentum of the particle are both described by the wave function $\psi(x,t)$. If we know the state of the particle at $t = 0$ ($\psi(x,0)$), we can compute its subsequent behavior by applying the *Schrodinger Equation*

$$\frac{d\psi}{dt} = -\frac{i}{\hbar}\hat{H}\psi$$

The operator $\hat{H}$ is called the *Hamiltonian* and plays a crucial role in quantum mechanics. The Hamiltonian can be computed once we have a complete knowledge of the particle's interactions, and the *laws that govern those interactions* — the laws that tell us how to construct the Hamiltonian. Just like with Newton's Second Law, the Schrodinger Equation is incomplete without those laws, but the Schrodinger Equation by itself has physical content: the laws that tell us how to construct the Hamiltonian should be *simple*. In quantum mechanics, it is the *Schrodinger Equation* that sets the program for studying nature.

- In order to gain some insight into these laws, it would help for us to understand what quantity (if any) the Hamiltonian operator represents. To do this, imagine that we have a situation where the wave function has a definite *frequency*:

$$\psi(x,t) = \psi(x)e^{-i\omega t}$$

Such states are called *stationary states* because the probability density does not depend on time

$$P(x,t) = |\psi(x,t)|^2 = |\psi(x)e^{-i\omega t}|^2 = |\psi(x)|^2$$

If we apply the Schrodinger Equation to such states, we obtain

$$\hat{H}\psi(x,t) \;=\; -\frac{\hbar}{i}\frac{d\psi}{dt}$$

$$
\begin{aligned}
&= -\frac{\hbar}{i}\psi(x)\frac{d}{dt}(e^{-i\omega t}) \\
&= -\frac{\hbar}{i}\psi(x)(-i\omega)e^{-i\omega t} \\
&= \hbar\omega\psi(x,t)
\end{aligned}
$$

The Hamiltonian represents the quantity $\hbar\omega$ which, according to de Broglie, is the *total energy* of the particle. It should actually make sense that stationary states have definite energy; if $\Delta E = 0$, then (according to the uncertainty principle), $\Delta t = \infty$: such states should last *forever*.

- Normally when we study the "motion" of a particle using the Schrodinger Equation, we find the stationary states and their corresponding values of energy by solving the *time-independent Schrodinger Equation*

$$\hat{H}\psi_n(x) = E_n\psi_n(x)$$

It is then understood that the complete time-dependent state is given by

$$\psi_n(x,t) = \psi_n(x)e^{-i\omega_n t} \qquad \omega_n = E_n/\hbar$$

- Normally we are content with finding the stationary states and their corresponding energies. However, if we are actually interested in solving for the time development of a general initial state $\psi(x,0)$, we first write it as a linear combination of stationary states (there are theorems that say this is always possible):

$$\psi(x,0) = \sum_n c_n\psi_n(x)$$

The complete time-dependent state is then given by

$$\psi(x,t) = \sum_n c_n\psi_n(x)e^{-i\omega_n t}$$

If two or more states with different energy (and hence different frequency) are combined, there will be interference among these various wave functions which depends on time, and the probability density $P(x,t)$ will depend on time in a manner that can now be calculated.

- A simple non-relativistic particle moving in one dimension and subject to conservative (position-dependent) forces has a total energy

$$E = K + U = \frac{p^2}{2m} + U(x)$$

Thus, it makes sense that the Hamiltonian operator should be

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)$$

The time-independent Schrodinger Equation reduces to

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi(x) = E\psi(x)$$

This is the form of the Schrodinger Equation we will use for most of the rest of this chapter.

The free particle

- A free particle is a particle with no forces acting on it. For such a particle, $U(x)$ is a constant which we may as well set to zero. The time-independent Schrodinger Equation reduces to

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi(x)$$

which can be rewritten

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

- This is an example of a linear (second-order) differential equation with constant coefficients. The standard procedure for solving such problems is to assume a solution of the form

$$\psi(x) = e^{\alpha x}$$

Plugging this into the differential equation reduces that equation into an algebraic one: derivatives are replaced by factors of α:

$$(\alpha^2 + 2mE/\hbar^2)\psi(x) = 0$$

Either $\psi(x) = 0$ for all x (a non-interesting solution), or else

$$\alpha^2 + \frac{2mE}{\hbar^2} = 0$$

The quadratic equation has two solutions

$$\alpha_\pm = \pm\sqrt{-\frac{2mE}{\hbar^2}}$$

leading to two independent solutions to the original differential equation:

$$\psi_+(x) = e^{\alpha_+ x} \qquad \psi_-(x) = e^{\alpha_- x}$$

Since the differential equation is linear, linear combinations of solutions are themselves solutions, so the general solution is

$$\psi(x) = A_+ e^{\alpha_+ x} + A_- e^{\alpha_- x}$$

- For $E \geq 0$ (the physically relevant case), the values of α are imaginary and can be written $\pm ik$, where $k = \sqrt{2mE/\hbar^2}$. The general solution can be written

  $$\psi(x) = A_+ e^{ikx} + A_- e^{-ikx}$$

  This represents a particle travelling with momentum $p = \hbar k = \sqrt{2mE}$ in either of two directions, or a superposition of both.

- Note that the general solution can also be written in the form

  $$\psi(x) = B\cos(kx) + C\sin(kx)$$

  This form of the solution jumbles together the two possible directions of momentum, and is not as useful in this case, although it will be the form of choice later when we consider the standing-wave solutions to the particle in a box.

- For a given wave number k, the solution $\psi_k(x) = Ae^{ikx}$ has an energy $E_k = \hbar^2 k^2/(2m)$. The full time dependence of this stationary state is given by

  $$\psi_k(x,t) = \psi_k(x)e^{-i\omega_k t} = Ae^{i(kx-\omega_k t)} \qquad \omega_k = E_k/\hbar = \hbar k^2/(2m)$$

- If we are interested in the time development of a general initial state $\psi(x,0)$, we first express that state as a linear combination of solutions to the time-independent Schrodinger Equation:

  $$\psi(x,0) = \int_{-\infty}^{\infty} A(k)e^{ikx}\,dk$$

The coefficients $A(k)$ can be calculated by using the Fourier transform:

$$A(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \psi(x,0)e^{-ikx}\,dx$$

The full time-dependent solution is then given by

$$\psi(x,t) = \int_{-\infty}^{\infty} A(k)e^{ikx}e^{-i\omega_k t}\,dk = \int_{-\infty}^{\infty} A(k)e^{i(kx-\omega_k t)}\,dk$$

The Schrodinger Equation has basically allowed us to recover the full time-dependent wave packet solution, and has established the dispersion relationship between ω and k.

- What if $E < 0$? Are there any solutions in that case? Well, yes and no. In this case, the two values of α are real and can be written $\pm\kappa$, where $\kappa = \sqrt{2m(-E)/\hbar^2}$. The general solution can be written

$$\psi(x) = A_+e^{\kappa x} + A_-e^{-\kappa x}$$

For a given value of κ (positive or negative), the solution $\psi_\kappa(x) = Ae^{\kappa x}$ has an energy $E_\kappa = -\hbar^2\kappa^2/(2m)$.

- The problem with these solutions is that they blow up. If $\kappa > 0$, then $\psi_\kappa(x) \to \infty$ as $x \to \infty$. If $\kappa < 0$, then $\psi_\kappa(x) \to \infty$ as $x \to -\infty$. Either way, $\psi_\kappa(x)$ is unbounded and cannot represent the probability distribution of a particle.

- To be fair, $\psi_k(x) = Ae^{ikx}$ by itself cannot represent the state of a particle either, because the wave function cannot be normalized. However, we can construct localized wave packets from linear combinations of $\psi_k(x)$ which *can* be normalized, and $\psi_k(x)$ itself can be thought of as a wave packet in the limit $\sigma_k \to 0$ (or $\sigma_x \to \infty$). However, there is no way to construct a linear combination of wave functions of the form $\psi_\kappa(x) = Ae^{\kappa x}$ that will lead to bounded, normalizable wave packets.

The particle in a box

- For a free particle, the energy spectrum (i.e., set of allowed values of energy) turns out to be continuous. All values $E \geq 0$ yielded a solution

to the time-independent Schrodinger Equation, and thus represent allowed values of energy. Such will not be the case for the particle in the box. It turns out that, in general, when a particle is essentially confined by forces to a finite region, the corresponding energy spectrum is no longer continuous. Only certain discrete energies (usually characterized by some sort of integer *quantum number*) are allowed.

- Consider the case of a particle in a (1D) box. The potential energy function associated with this particle is as follows

$$U(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq L \\ \infty & \text{if } x < 0 \text{ or } x > L \end{cases}$$

The "box" is the region $0 \leq x \leq L$. There are no forces on the particle when it is in that region ($U(x)$ is constant). Outside of that region, however, the potential energy of the particle is ∞, essentially forbidding the particle from ever entering that region.

- The time-independent Schrodinger Equation is given by

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi(x) = E\psi(x)$$

Since $U(x)$ is given by different formulas in different regions, it makes sense to solve this equation in each region separately, and then combine the solutions into one wave function. Indeed, that is what we will do.

- For the intervals $x < 0$ and $x > L$ where $U(x) = \infty$, it turns out that the wave function must vanish ($\psi(x) = 0$). This makes sense on physical grounds (the particle cannot exist in such a region, even for a short time, if there is an infinite energy deficit), and also on mathematical grounds (if $U(x) = \infty$, then the term $U(x)\psi(x)$ can only be finite if $\psi(x) = 0$).

- For the interval $0 \leq x \leq L$ where $U(x) = 0$, we use the free particle solution

$$\psi(x) = A_+ e^{ikx} + A_- e^{-ikx} = B\cos(kx) + C\sin(kx) \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

The complete solution in all three regions is thus given by

$$\psi(x) = \begin{cases} B\cos(kx) + C\sin(kx) & \text{if } 0 \leq x \leq L \\ 0 & \text{if } x < 0 \text{ or } x > L \end{cases}$$

The energy associated with this stationary state is given by $E = \hbar^2 k^2/(2m)$.

- It appears that, once again, all energy values $E \geq 0$ are allowed. However, when we splice solutions in different regions together to obtain an overall solution to the Schrodinger Equation, we need to be careful. In order for the Schrodinger Equation to be valid at the boundary points, *we need to impose continuity conditions on the wave function.* The time-independent Schrodinger Equation can be rewritten

$$\frac{d^2\psi}{dx^2} = -\frac{2m(E - U(x))}{\hbar^2}\psi(x)$$

  In the absence of infinities, this equation requires $d^2\psi/dx^2$ to be finite at all points, which requires *both $\psi(x)$ and $d\psi/dx$ to be continuous at all points, including any boundary points between different regions.*

- In this particular case, $U \to \infty$ as we cross into the forbidden regions, and so there will be a jump discontinuity in the value of $d\psi/dx$ at $x = 0$ and $x = L$. However, $\psi(x)$ must still be continuous at those points. In order for this to be the case, both $\psi(0)$ and $\psi(L)$ must be zero.

- Note that this restriction on $\psi(x)$ is similar to the restriction we place on ordinary waves (e.g., waves on a string) when they are confined between two fixed points. It will lead to the same physical result: *an integer number of half-wavelengths must fit within the region* $[0, L]$: $n\lambda/2 = L$.

- Let's start by imposing $\psi(0) = 0$.

$$\psi(0) = B\cos(0) + C\sin(0) = B(1) + C(0) = B$$

  Imposing $\psi(0) = 0$ forces $B = 0$, causing us to reject the cosine term. Therefore, the wave function in the region $0 \leq x \leq L$ is reduced to

$$\psi(x) = C\sin(kx)$$

  If we now impose the condition that $\psi(L) = 0$, we determine that $C\sin(kL) = 0$. This either requires $C = 0$ (giving us $\psi(x) = 0$ everywhere, a non-solution) or else $kL = n\pi$. Thus, only certain values of k are allowed, namely $k_n = n\pi/L$. Note that this is equivalent to $n\lambda_n/2 = L$, as claimed earlier.

- The complete solution can now be written

$$\psi_n(x) = \begin{cases} C_n\sin(k_n x) & \text{if } 0 \leq x \leq L \\ 0 & \text{if } x < 0 \text{ or } x > L \end{cases}$$

where

$$k_n = \frac{n\pi}{L} \qquad E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2}\, n^2 = E_0 n^2$$

Note that the energy spectrum in this case is discrete. Only certain energies are allowed.

- To normalize the wave functions, we set $\int_{-\infty}^{\infty} |\psi_n(x)|^2\, dx = 1$ and solve for C_n. We get

$$1 = \int_{-\infty}^{\infty} |\psi_n(x)|^2\, dx = \int_0^L |C_n|^2 \sin^2(k_n x)\, dx = |C_n|^2 L \langle \sin^2(k_n x) \rangle = |C_n|^2 L/2$$

and so $C_n = \sqrt{2/L}$ (possibly multiplied by an arbitrary phase $e^{i\phi}$).

- (Draw graphs for both $\psi_n(x)$ and $P(x) = |\psi_n(x)|^2$ for $n = 1$, 2, and 3. See Ch5:p1.) The lowest energy state is $n = 1$ and has zero intermediate nodes. Each subsequent value of n leads to a higher energy excited state, and adds one additional node to the wave function. This same behavior occurs for just about *any* potential energy function $U(x)$ which essentially confines a particle to a finite region of space, and can be understood in terms of the time-independent Schrodinger Equation:

$$\frac{d^2\psi}{dx^2} = -\frac{2m(E - U(x))}{\hbar^2}\psi(x)$$

Note that as E increases, the negative coefficient on the right-hand side increases, causing a larger curved bend of the wave function back towards zero. As E is increased more and more, more zero crossings will result. Notice that if we are not careful about the choice of E, the final node might not occur at $x = L$ like it is supposed to. This spells disaster for the wave function when $U(x)$ jumps to infinity (see Ch5:p1). We will have more to say about this when we consider the finite well potential.

- Note that the ground state energy E_0 is not zero, and is given by

$$E_0 = \frac{\hbar^2 \pi^2}{2mL^2}$$

As L decreases, the value of E_0 increases. This can be understood in terms of the uncertainty principle. The more one tries to confine a particle, the greater uncertainty one has for its momentum, and thus the

greater its kinetic energy is expected to be. Note also that the excited state energy $E_n = E_0 n^2$ of the original length box is equivalent to the ground state energy of a box of length $L_n = L/n$. This makes sense, since the excited state wave function has nodes spaced L/n apart. It is as if one places additional walls where the nodes of the wave function are.

- The wave functions can be used to calculate expectation values. The results are as follows:

$$\langle x \rangle = \frac{2}{L} \int_0^L x \sin^2(k_n x)\, dx = \frac{L}{2}$$

$$\langle x^2 \rangle = \frac{2}{L} \int_0^L x^2 \sin^2(k_n x)\, dx = L^2 \left(\frac{1}{3} - \frac{1}{2\pi^2 n^2} \right)$$

$$\langle p \rangle = \frac{2}{L} \int_0^L \sin(k_n x) \frac{\hbar}{i} \frac{d}{dx} \sin(k_n x)\, dx = 0$$

$$\langle p^2 \rangle = \frac{2}{L} \int_0^L \sin(k_n x) \frac{\hbar^2}{i^2} \frac{d^2}{dx^2} \sin(k_n x)\, dx = \hbar^2 k_n^2$$

The uncertainties for x and p can now be calculated

$$\delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \frac{L}{\sqrt{12}} \sqrt{1 - \frac{6}{\pi^2 n^2}}$$

$$\delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \hbar k_n = \frac{\hbar n \pi}{L}$$

The uncertainty relationship is

$$(\delta x)(\delta p) = \hbar \sqrt{\frac{n^2 \pi^2}{12} - \frac{1}{2}}$$

Note that $\pi^2/12 > 9/12 = 3/4$ and so $(\delta x)(\delta p)$ always exceeds $\hbar/2$.

- Once again, the stationary states can be used to determine the time evolution of a general initial state $\psi(x, 0)$. A general initial state can be expressed as a linear combination of the allowed stationary states, as follows:

$$\psi(x, 0) = \sum_{n=1}^{\infty} A_n \psi_n(x) = \sqrt{2/L} \sum_{n=1}^{\infty} A_n \sin(k_n x)$$

This is the discrete Fourier transform appropriate for wave functions defined over the finite length interval $[0, L]$ which vanish at the end points. The full time-dependent wave function would then be given by

$$\psi(x,t) = \sqrt{2/L} \sum_{n=1}^{\infty} A_n \sin(k_n x) e^{-i\omega_n t} \qquad \omega_n = E_n/\hbar$$

Constructing a wave packet that is narrow compared to L should require the use of a large number of high n stationary states. Time evolving such a wave packet will show that wave packet bounce back and forth as the particle collides with the boundaries of the box. This is the expected classical behavior of such a particle.

The finite well potential

- The infinite well potential that we considered last time to model the particle in a box is actually a limiting case of the finite well potential that we consider now.

$$U(x) = \begin{cases} 0 & \text{if } -L/2 \le x \le L/2 \\ U_0 & \text{if } |x| > L/2 \end{cases}$$

  Here we are considering energies for which $0 \le E \ll U_0$.

- Technical note: we shifted the box region from $[0, L]$ to $[-L/2, L/2]$. This is for convenience only: it has no physical significance.
  - The main advantage of using $[0, L]$ before is that allowed us to place one of the nodes at $x = 0$. That will no longer happen.
  - The main advantage of using $[-L/2, L/2]$ now is it will allow us to take advantage of symmetry. That will be especially important now with U_0 finite because this calculation is more involved.

- First obvious question: if $E < U_0$, does it really matter if U_0 is finite? After all, in classical physics, a particle is unable to reach any point where $E < U(x)$. The actual value of $U(x)$ at such points should not affect the motion of that particle. However, in quantum mechanics, the situation is different because of the energy-time uncertainty principle. It is possible to violate energy conservation for short periods of time. Thus,

we should expect the wave function to penetrate the forbidden region. The penetration depth will depend on U_0, and is expected to vanish as $U_0 \to \infty$. One of the reasons for studying the finite well potential is to gain additional insight as to what happens when $U_0 \to \infty$.

- Without further hesitation, here are the solutions to the time-independent Schrodinger Equation in each region:

$$\psi(x) = \begin{cases} A_+ e^{ikx} + A_- e^{-ikx} & \text{if } -L/2 \le x \le L/2 \\ B_- e^{-\kappa x} & \text{if } x > L/2 \\ C_+ e^{\kappa x} & \text{if } x < -L/2 \end{cases}$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}} \qquad \kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$

These solutions can be obtained from the free particle solutions derived earlier. The forbidden region solutions are energy shifted versions of the $E < 0$ "solutions" we obtained for the free particle.

- Note that the $B_+ e^{\kappa x}$ term for $x > L/2$ and the $C_- e^{-\kappa x}$ term for $x < -L/2$ are not present in the solution above. They are rejected because including them would cause $\psi(x)$ to diverge in the limit $x \to \pm\infty$. The other two exponential terms that we do include do *not* diverge, but instead approach zero exponentially as $x \to \pm\infty$. The average penetration depth of the wave function into the forbidden region is given by the "space constant" $1/(2\kappa)$ (the 2 comes from squaring the wave function to get the probability density), which goes to zero as $U_0 \to \infty$. Notice also that $1/(2\kappa)$ is proportional to $\hbar$, which explains why we don't observe this sort of barrier penetration in classical physics.

- The next task is to determine the coefficients $A_\pm$, B_-, and C_+, and also determine the allowed values of k (as well as κ and E). Since $U(x)$ does not reach ∞ this time, we will need to impose continuity conditions on $\psi(x)$ and $d\psi/dx$ at both $x = L/2$ and $x = -L/2$. This task can be facilitated by taking advantage of symmetry, which we now discuss.

- It turns out that because $U(-x) = U(x)$, the stationary states must either be even or odd functions:

$$\psi(-x) = \psi(x) \ \text{(even)} \qquad \text{OR} \qquad \psi(-x) = -\psi(x) \ \text{(odd)}$$

To establish this fact, we would first show that if $\psi(x)$ is a solution to the time-independent Schrodinger Equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi(x) = E\psi(x)$$

then so is $\psi(-x)$. Once that is done, we are left with two possibilities: (1) either $\psi(-x)$ and $\psi(x)$ are linearly dependent, which forces $\psi(-x) = \pm\psi(x)$ (i.e., $\psi(x)$ itself is either even or odd), or else (2) $\psi(x)$ and $\psi(-x)$ represent two independent solutions to the time-independent Schrodinger Equation with the same energy. In that case, we can replace $\psi(x)$ and $\psi(-x)$ with two other independent solutions:

$$\psi_+(x) = \frac{\psi(x) + \psi(-x)}{2} \qquad \psi_-(x) = \frac{\psi(x) - \psi(-x)}{2}$$

In this case, $\psi_+(x)$ is even and $\psi_-(x)$ is odd.

- This result is actually a special case of a more general symmetry principle: If the Hamiltonian is symmetric under some symmetry operation ($x \to -x$ in this case), then the stationary states should be symmetric under the same operation. It is important to note that kinetic energy is also symmetric under $x \to -x$. In more advanced treatments of quantum mechanics, this principle would be expressed in terms of operators.

- Even wave functions: Since $\psi(-x) = \psi(x)$, we have $A_+ = A_- = \frac{1}{2}A$ and $B_- = C_+ = B$. The wave function can be rewritten

$$\psi(x) = \begin{cases} A\cos(kx) & \text{if } |x| \le L/2 \\ Be^{-\kappa|x|} & \text{if } |x| > L/2 \end{cases}$$

Continuity of $\psi(x)$ and $d\psi/dx$ at $x = L/2$ (and $x = -L/2$) leads to the following:

$$A\cos(\tfrac{1}{2}kL) = Be^{-\frac{1}{2}\kappa L}$$

$$-kA\sin(\tfrac{1}{2}kL) = -\kappa Be^{-\frac{1}{2}\kappa L}$$

Dividing these two equations yields

$$k\tan(\tfrac{1}{2}kL) = \kappa$$

which allows us (in principle) to solve for allowed values of E (k and κ depend on E and other known constants). In general, this would require

numerical solution methods, but if we assume that $E \ll U_0$, then the above equation basically boils down to

$$\tan(\tfrac{1}{2}kL) = \text{a large positive number}$$

$$\tfrac{1}{2}kL \lesssim \pi/2 + n\pi$$

$$k_{2n+1} \lesssim \frac{(2n+1)\pi}{L}$$

- Odd wave functions: Since $\psi(-x) = -\psi(x)$, we have $A_+ = -A_- = \frac{1}{2i}A$ and $B_- = -C_+ = B$. The wave function can be rewritten

$$\psi(x) = \begin{cases} A\sin(kx) & \text{if } |x| \le L/2 \\ Be^{-\kappa x} & \text{if } x > L/2 \\ -Be^{\kappa x} & \text{if } x < -L/2 \end{cases}$$

Continuity of $\psi(x)$ and $d\psi/dx$ at $x = L/2$ leads to the following:

$$A\sin(\tfrac{1}{2}kL) = Be^{-\frac{1}{2}\kappa L}$$

$$kA\cos(\tfrac{1}{2}kL) = -\kappa Be^{-\frac{1}{2}\kappa L}$$

Dividing these two equations yields

$$k\cot(\tfrac{1}{2}kL) = -\kappa$$

Again, if we assume that $E \ll U_0$, then the above equation implies

$$\cot(\tfrac{1}{2}kL) = \text{a large negative number}$$

$$\tfrac{1}{2}kL \lesssim n\pi$$

$$k_{2n} \lesssim \frac{(2n)\pi}{L}$$

- To complete the solutions above, we should solve for B in terms of A from the one of the boundary condition equations, and then solve for A by imposing the normalization condition on the entire wave function. This would be done separately for even and odd wave functions.

- Combining the even and odd wave function results together, the allowed values of k are

$$k_n \lesssim \frac{n\pi}{L}$$

As $U_0 \to \infty$, the inequality approaches equality and we recover the standing wave solutions for the infinite potential well. For U_0 finite, the value of k_n comes up slightly short, resulting in a wave function that doesn't quite reach 0 at $x = \pm L/2$. The exponential decay takes over after that and drives $\psi(x)$ to zero very quickly as $x \to \pm\infty$. See Ch5:p1 for pictures (depicting both an even and an odd wave function).

- It is possible to construct wave packet solutions by expanding the initial state $\psi(x, 0)$ in terms of the stationary states:

$$\psi(x, 0) = \sum_{n=1}^{\infty} A_n \psi_n(x)$$

The full time dependence would be given by

$$\psi(x, t) = \sum_{n=1}^{\infty} A_n \psi_n(x) e^{-i\omega_n t} \qquad \omega_n = \frac{E_n}{\hbar} = \frac{\hbar k_n^2}{2m}$$

The result would be a wave packet travelling at the group velocity, and bouncing back and forth within the box. Each time the wave packet encounters one of the boundaries, it would penetrate the forbidden region slightly (average depth $1/(2\kappa)$) before bouncing back into the box region.

The simple harmonic oscillator

- The simple harmonic oscillator is one of the most important mechanical systems that can be studied, because it can be solved exactly (both classically and quantum mechanically), and is a very good approximation to a great many phenomena, all the way from spring-mass and pendulum systems (classical) to atomic and nuclear vibrations (quantum).

- In classical physics, simple harmonic motion results when a mass m experiences a net linear restoring force $F = -kx$ which attempts to return that mass to its equilibrium point (which is normally taken to be $x = 0$). Newton's Second Law takes the form

$$m\frac{d^2x}{dt^2} + kx = 0$$

which can be solved for $x(t)$. The general solution is sinusoidal

$$x(t) = A\cos(\omega_0 t - \phi)$$

where A is the amplitude, $\omega_0 = \sqrt{k/m}$ is the natural (angular) frequency of oscillation, and ϕ is an arbitrary phase. The linear restoring force is conservative, with a corresponding potential energy given by

$$U(x) = \tfrac{1}{2}kx^2 = \tfrac{1}{2}m\omega_0^2 x^2$$

Total mechanical energy of the oscillation is given by

$$E = K + U = \tfrac{1}{2}m\omega_0^2(A\cos(\omega_0 t - \phi))^2 + \tfrac{1}{2}m(-A\omega_0\sin(\omega_0 t - \phi))^2 = \tfrac{1}{2}kA^2$$

Mechanical energy is conserved and is proportional to A^2. All of this should be familiar.

- The time-independent Schrodinger Equation for the harmonic oscillator is given by

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega_0^2 x^2\psi(x) = E\psi(x)$$

using the potential energy function given above (ω_0 is the classical oscillation angular frequency).

- The above equation can be simplified by applying the principles of dimensional analysis. To that end, we replace x and E with dimensionless parameters η and ϵ, respectively:

$$x = a_0\eta \qquad E = E_0\epsilon$$

After substituting the values of x and E above into the Schrodinger Equation, we get

$$-\frac{\hbar^2}{2ma_0^2}\frac{d^2\psi}{d\eta^2} + \frac{1}{2}m\omega_0^2 a_0^2\eta^2\psi(\eta) = E_0\epsilon\psi(\eta)$$

Since η and ϵ are dimensionless and $d^2\psi/d\eta^2$ has the same dimensions as $\psi(\eta)$, the three coefficients

$$\frac{\hbar^2}{2ma_0^2} \propto \frac{1}{2}m\omega_0^2 a_0^2 \propto E_0$$

should all be proportional to each other (the proportionality constants are pure numbers and can be chosen arbitrarily). This will allow us to solve for the length and energy scale parameters, a_0 and E_0, and then divide out a common factor leaving just dimensionless quantities in the Schrodinger Equation.

- Equating the first two coefficients and solving for a_0 yields

$$\hbar^2 \propto m^2\omega_0^2 a_0^4$$

$$a_0 \propto \sqrt{\frac{\hbar}{m\omega_0}}$$

$$a_0 = \sqrt{\frac{\hbar}{2m\omega_0}}$$

The proportionality constant $1/\sqrt{2}$ is chosen so that δx turns out to be a_0 for the ground state. The first two coefficients now simplify:

$$\frac{\hbar^2}{2ma_0^2} = \frac{\hbar^2}{2m}\frac{2m\omega_0}{\hbar} = \hbar\omega_0 = E_0$$

$$\frac{1}{2}m\omega_0^2 a_0^2 = \frac{1}{2}m\omega_0^2\frac{\hbar}{2m\omega_0} = \frac{1}{4}\hbar\omega_0 = \frac{1}{4}E_0$$

where $E_0 = \hbar\omega_0$ is chosen arbitrarily. We now plug all this into the Schrodinger Equation and then divide out E_0 to obtain

$$-\frac{d^2\psi}{d\eta^2} + \frac{1}{4}\eta^2\psi(\eta) = \epsilon\psi(\eta)$$

- For any given energy E, the classical turning points $\pm x_0$ are defined so that $U(\pm x_0) = E$ ($x_0 = (2\sqrt{\epsilon})a_0$). According to classical mechanics, the particle cannot go outside of the region $[-x_0, x_0]$. If the potential energy were to flatten out after that to some limiting value $U_0 > E$, then the quantum mechanical wave function should be expected to be proportional to $e^{-\kappa|x|}$ for some κ when $|x|$ is large. However, the potential energy continues to increase as x increases, and so the wave function should decay faster than a simple exponential.

- It is reasonable to try a Gaussian

$$\psi(\eta) = Ae^{-\beta\eta^2}$$

If we plug that into the equation above, we find that it works, as long as β and ϵ are set to the correct values. To show this, we first evaluate the derivatives of $\psi(\eta)$.

$$\frac{d\psi}{d\eta} = -2\beta\eta\psi(\eta)$$

$$\frac{d^2\psi}{d\eta^2} = (-2\beta + 4\beta^2\eta^2)\psi(\eta)$$

Comparing this to the differential equation above, we see that $\psi(\eta)$ is a solution provided that

$$2\beta = \epsilon \qquad 4\beta^2 = \tfrac{1}{4}$$

Solving for β and ϵ yields

$$\beta = \tfrac{1}{4} \qquad \epsilon = \tfrac{1}{2}$$

After plugging this into the wave function, reintroducing the dimensional scales, and normalizing the wave function, we find that

$$\psi(x) = (2\pi)^{-1/4} a_0^{-1/2} e^{-x^2/(4a_0^2)}$$

is a stationary state corresponding to the energy

$$E = \tfrac{1}{2}\hbar\omega_0$$

The state is a Gaussian centered at $x = 0$ (the equilibrium point) and $\delta x = a_0$ (recall that we chose a_0 so that this would happen). Based on the fact that this wave function has no intermediate nodes, it appears that this wave function defines the ground state of the harmonic oscillator.

- To obtain the higher energy stationary states, we need to find wave functions with intermediate nodes. The first thought might be to use sinusoidal functions like we did with the particle in a box, but this does not work too well. No matter how small we choose k, $e^{-x^2/(4a_0^2)}\sin(kx)$ will have infinitely many nodes. The solution turns out to be much simpler than that: nodes can be introduced by multiplying the Gaussian by a *polynomial*.

- The Schrodinger Equation can actually be solved systematically at this point. Since we now know that $\psi(\eta) \sim e^{-\eta^2/4}$ for large values of $|\eta|$, we can try the following

$$\psi(\eta) = (2\pi)^{-1/4} a_0^{-1/2} f(\eta) e^{-\eta^2/4}$$

The factor out front is based on the normalization of the ground state, and sets the units for $\psi(\eta)$ (i.e., $f(\eta)$ is dimensionless). Evaluating derivatives yields

$$\frac{d\psi}{d\eta} = (2\pi)^{-1/4} a_0^{-1/2} (f'(\eta) - \tfrac{1}{2}\eta f(\eta)) e^{-\eta^2/4}$$

$$\frac{d^2\psi}{d\eta^2} = (2\pi)^{-1/4} a_0^{-1/2} (f''(\eta) - \eta f'(\eta) - \tfrac{1}{2} f(\eta) + \tfrac{1}{4}\eta^2 f(\eta)) e^{-\eta^2/4}$$

Plugging this into the dimensionless Schrodinger Equation, cancelling out the overall factor of $(2\pi)^{-1/4} a_0^{-1/2} e^{-\eta^2/4}$, and performing some simplifications, yields

$$f''(\eta) - \eta f'(\eta) + (\epsilon - \tfrac{1}{2}) f(\eta) = 0$$

As a check, we see that $f(\eta) =$ constant is a solution if $\epsilon = \frac{1}{2}$, consistent with the ground state wave function.

- The differential equation for $f(\eta)$ can be solved by expanding it as a power series

$$f(\eta) = \sum_{k=0}^{\infty} b_k \eta^k$$

The derivatives can be evaluated term by term.

$$f'(\eta) = \sum_{k=1}^{\infty} k b_k \eta^{k-1} = \sum_{k=0}^{\infty} (k+1) b_{k+1} \eta^k$$

$$f''(\eta) = \sum_{k=1}^{\infty} k(k+1) b_{k+1} \eta^{k-1} = \sum_{k=0}^{\infty} (k+1)(k+2) b_{k+2} \eta^k$$

$$\eta f'(\eta) = \sum_{k=0}^{\infty} k b_k \eta^k$$

After taking the derivative, we reindex the sum, replacing $k-1$ with k, so that η is always raised to the k power in the sum. $\eta f'(\eta)$ is calculated directly from the first expression for $f'(\eta)$ (the $k = 0$ term is thrown

back in for consistency — it is zero anyway). Substituting this back into the differential equation yields the following:

$$\sum_{k=0}^{\infty}((k+1)(k+2)b_{k+2} - kb_k + (\epsilon - \tfrac{1}{2})b_k)\eta^k = 0$$

This power series vanishes if and only if each coefficient vanishes:

$$(k+1)(k+2)b_{k+2} - kb_k + (\epsilon - \tfrac{1}{2})b_k = 0$$

$$b_{k+2} = \frac{k - (\epsilon - \frac{1}{2})}{(k+1)(k+2)}\, b_k$$

This defines a recurrence relation that will allow us to solve for the coefficients b_k in the power series for $f(\eta)$.

- It appears for the moment that we have a viable solution for every possible value of E (or equivalently, ϵ). However, that is an illusion. The recurrence relation for large even index $2k$ reduces to $b_{2k+2} \sim b_{2k}/(2k+2)$, so that $b_{2k} \sim b_0/(2^k k!)$. Summing this series (even powers only) yields

$$f(\eta) \sim \sum_{k=0}^{\infty} \frac{1}{2^k k!}\eta^{2k} = e^{\eta^2/2}$$

which leads to $\psi(\eta) \sim e^{+\eta^2/4}$. This wave function diverges as $\eta \to \pm\infty$. The same problem arises with the odd terms in the power series.

- The only way to avoid this catastrophe is to truncate the power series (i.e., all coefficients beyond a certain value of k are zero). The good news is that once $b_k = 0$ for some k, all subsequent terms of the same parity (i.e., b_{k+2}, b_{k+4}, b_{k+6}, etc) will also vanish. So it is simply a question of going from a non-zero coefficient to a zero coefficient for one value of k.

- Suppose the series truncates at $k = n$, so that $f(\eta)$ is an n^{th} order polynomial. Then $b_n \neq 0$ and $b_{n+2} = 0$. This will require $n - (\epsilon - \frac{1}{2}) = 0$, which allows us to solve for ϵ (and hence, E):

$$\epsilon = n + \tfrac{1}{2} \qquad E = (n + \tfrac{1}{2})\hbar\omega_0$$

If n is even, then all terms $b_0, b_2, \ldots, b_n$ are proportional to b_0, which can be set by normalization. Since $k - (\epsilon - \frac{1}{2})$ can only vanish for one value of k (and that value happens to be n), all of the odd coefficients must vanish to begin with (i.e., $b_1 = b_3 = b_5 = \ldots = 0$). If n is odd, then $b_1, b_3, \ldots, b_n$ are non-zero and proportional to b_1, and $b_0 = b_2 = b_4 = \ldots = 0$.

- Evidently, the stationary states are of the form

$$\psi_n(x) = (2\pi)^{-1/4} a_0^{-1/2} f_n(x/a_0) e^{-x^2/(4a_0^2)} \qquad E_n = \hbar\omega_0(n + \tfrac{1}{2})$$

where $f_n(\eta)$ is a polynomial of order n and is either even or odd according to whether n is even or odd. Actually, this is to be expected: $U(-x) = U(x)$ for the harmonic oscillator, and so we should expect our stationary states to have definite parity (i.e., be an even or odd function). It should also be noted that order n polynomials in general have n zeros (i.e., there are n values of η for which $f_n(\eta) = 0$), and so the n^{th} stationary state has n nodes. This is to be expected.

- The first few polynomials are given by

$$\begin{aligned} f_0(\eta) &= b_0 \\ f_1(\eta) &= b_1\eta \\ f_2(\eta) &= b_0(1 - \eta^2) \\ f_3(\eta) &= b_1(\eta - \tfrac{1}{3}\eta^3) \\ f_4(\eta) &= b_0(1 - 2\eta^2 + \tfrac{1}{3}\eta^4) \end{aligned}$$

The corresponding (normalized) wave functions are

$$\begin{aligned} \psi_0(x) &= (2\pi)^{-1/4} a_0^{-1/2} e^{-x^2/(4a_0^2)} \\ \psi_1(x) &= (2\pi)^{-1/4} a_0^{-1/2} (x/a_0) e^{-x^2/(4a_0^2)} \\ \psi_2(x) &= (2\pi)^{-1/4} a_0^{-1/2} \tfrac{1}{\sqrt{2}}(1 - (x/a_0)^2) e^{-x^2/(4a_0^2)} \\ \psi_3(x) &= (2\pi)^{-1/4} a_0^{-1/2} \sqrt{\tfrac{3}{2}}(x/a_0 - \tfrac{1}{3}(x/a_0)^3) e^{-x^2/(4a_0^2)} \\ \psi_4(x) &= (2\pi)^{-1/4} a_0^{-1/2} \sqrt{\tfrac{3}{8}}(1 - 2(x/a_0)^2 + \tfrac{1}{3}(x/a_0)^4) e^{-x^2/(4a_0^2)} \end{aligned}$$

- Technical note on the normalization of these wave functions. A useful integral:

$$\int_{-\infty}^{\infty} (x/a_0)^n e^{-x^2/(2a_0^2)}\, dx = \gamma_n \sqrt{2\pi}\, a_0$$

where $\gamma_0 = 1$, $\gamma_1 = 0$ and $\gamma_{n+2} = (n+1)\gamma_n$. The first few non-zero values of γ_n:

$$\gamma_0 = 1 \quad \gamma_2 = 1 \quad \gamma_4 = 3 \quad \gamma_6 = 15 \quad \gamma_8 = 105$$

The appropriate value of b_0 or b_1 (as the case may be) can now be determined by first expanding $f_n(\eta)^2$ as a polynomial in η^2:

$$f_n(\eta)^2 = b_{0,1}^2(c_0 + c_2\eta^2 + c_4\eta^4 + \ldots)$$

Now the normalization integral can be computed:

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx \\ &= \int_{-\infty}^{\infty} (2\pi)^{-1/2} a_0^{-1} b_{0,1}^2 (c_0 + c_2(x/a_0)^2 + c_4(x/a_0)^4 + \ldots) e^{-x^2/(2a_0^2)} \, dx \\ &= b_{0,1}^2 (c_0\gamma_0 + c_2\gamma_2 + c_4\gamma_4 + \ldots) \end{aligned}$$

This can be solved for $b_{0,1}$.

- Note that the energy levels are given by

$$E_n = (n + \tfrac{1}{2})\hbar\omega_0$$

The separation between energy levels is a constant:

$$\Delta E = E_{n+1} - E_n = \hbar\omega_0$$

This is an interesting value for ΔE, because if one considers an electric charge oscillating with angular frequency ω_0, one might expect that charge to radiate EM radiation at that same frequency. The energy of that radiation is quantized: each photon has an energy $\hbar\omega_0$. Thus, each time the charge radiates one photon, it drops one energy level until it reaches the ground state.

- Note that the ground state energy E_0 is *not* zero. This is required by the uncertainty principle. Since $\delta x = a_0 < \infty$, $\delta p > 0$, and so there has to be some non-zero amount of kinetic energy in the ground state.

- Once again, a general initial state $\psi(x, 0)$ can be expressed as a superposition of stationary states:

$$\psi(x, 0) = \sum_{n=0}^{\infty} A_n \psi_n(x)$$

The full time evolution of this state is given by

$$\psi(x, t) = \sum_{n=0}^{\infty} A_n \psi_n(x) e^{-i\omega_n t} \qquad \omega_n = E_n/\hbar = (n + \tfrac{1}{2})\omega_0$$

If one considers a wave packet in the classical limit (i.e., by using very high n stationary states), one should be able to recover the classical

behavior of the harmonic oscillator. For example, it should be possible to show that

$$m\frac{d^2}{dt^2}\langle x\rangle = -k\langle x\rangle$$

where $k = m\omega_0^2$ is the spring constant.

Steps and barriers

- Imagine the following situation: a particle (or stream of particles) coming from $x = -\infty$ is travelling in the $+x$ direction as a free particle ($U = 0$) until it approaches $x = 0$ when it encounters forces ($U \neq 0$). In other words, suppose

$$U(x) = \begin{cases} 0 & \text{if } x < 0 \\ \text{something else} & \text{if } x > 0 \end{cases}$$

  What happens to the particle (or particles) in this case? Do they transmit all the way to $x = +\infty$? Do they reflect back to $x = -\infty$? If they reflect back, how far do they penetrate into the region where $U(x) \neq 0$? Can they somehow get trapped in a finite region of space, unable to escape to $x = \pm\infty$? All of these are interesting questions that we attempt to address with the help of the Schrodinger Equation.

- First of all, it pays to recall what classical physics predicts.
  - If $U(x) < E$ for all $x > 0$, then the particle may speed up or slow down as it travels along, but it will never stop, and cannot turn around. Such particles will always transmit through to $+\infty$.
  - If $U(x) \geq E$ for some points $x > 0$, then the particle will stop at the first turning point x_0, where $U(x_0) = E$. Assuming that U continues to increase at that point, the particle will start moving in the opposite direction and will reflect back to $-\infty$ in the exact reverse motion.
  - As far as getting trapped in a finite region of space, this cannot happen unless non-conservative forces also act, allowing the mechanical energy to decrease while the particle is travelling between two local maxima of $U(x)$. It may happen that the particle will lose enough mechanical energy while it is in that region that it can no longer escape.

- The closest we can come to "trapping" the particle with conservative forces is to have the first turning point occur at an unstable equilibrium (where U is a local maximum). In that case, it will take infinite time for the particle to reach the turning point, and if it ever got there, it would never move again. This case is impractical, since *any* fluctuation will upset the balance and cause the particle to start moving again in one direction or the other.
- In all cases, classical physics makes a definite prediction of what happens to the particle. Given the initial position, initial velocity, and complete information about the particle's interactions (by specifying $U(x)$), all subsequent motion is completely determined.

• Quantum mechanics makes very different predictions.

- It is quite likely that some particles will transmit to $+\infty$ whereas other particles will reflect back to $-\infty$, even if they all start off with the same energy and experience the same interactions. Quantum mechanics does *not* make definite predictions about the motions of specific particles; quantum mechanics only makes predictions regarding *probabilities*.
- Even if $U(x) < E$ for all $x > 0$, it is quite likely for some particles to reflect back to $-\infty$. In fact, this reflection can occur even if $U(x)$ *decreases* (implying a force in the $+x$ direction). Reflection can occur at any point where $U(x)$ changes.
- Even if $U(x) > E$ over some finite region $[a, b]$, it is quite possible for particles to "tunnel through" the barrier region and continue on to $+\infty$.
- The only way to stop all transmission to $+\infty$ is to have an infinite barrier, either in terms of height ($U \to \infty$) or length ($U(x) > E$ for all $x > a$). In the latter case, the particle can still penetrate the barrier for some distance before reflecting back (i.e., $\psi(x) \neq 0$ for at least some region beyond a).
- In quantum mechanics, it is very difficult to trap a particle in a finite region, even more so than in classical physics, because of the added possibility of tunnelling. Basically, $U(x)$ would have to go to $+\infty$ at some point or remain above E "forever" on *both* sides of that region

for the particle to remain trapped there. It is certainly going to be the case that any region a particle can get *into*, it can get out of again.

- Much of this behavior, such as reflecting off of "penetrable" barriers or transmitting through "impenetrable" barriers can occur with other waves. For example, light waves can reflect off of glass, even though light can travel through glass. Furthermore, if light attempts to cross a boundary into a region of lower index of refraction at an angle beyond the critical angle, total internal reflection is supposed to occur. But if there is another material just beyond the interface with a high enough index of refraction, some of the light might "tunnel through" the low index region to the other side. This is depicted in Fig. 5.28[5.22] on p. 163[166] (Fig. 5.23 on p. 167 of the 2nd edition shows this effect with water waves; unfortunately this figure was not carried over to the 3rd edition of the textbook).

- Consider for the moment a free particle ($U(x) = 0$ everywhere). The state

$$\psi(x) = Ae^{ikx}$$

describes a particle with a definite value of momentum $\hbar k$ in the $+x$ direction. Actually, this wave function cannot be normalized, but one can create a wave packet by combining such waves over a finite range of k values in order to describe the motion of a single particle in a manner consistent with the uncertainty principle. Alternatively, one can regard this wave function as describing the propagation of a *stream* of particles with a (linear) number density equal to

$$\rho = |\psi(x)|^2 = |A|^2$$

- This stream of particles is moving to the right with velocity

$$v = v_g = \hbar k/m$$

Even though we are not necessarily constructing a wave packet, it is still appropriate to use the group velocity v_g to determine the speed of these particles. We can now define the particle *current* at a given point x to be the net rate in which particles flow past this point in the $+x$ direction.

This current is related to particle number density and velocity in the usual way

$$J(x) = \rho v = |\psi(x)|^2 v_g = |A|^2 \hbar k/m$$

For a more general wave function, one can show that

$$J(x) = \Re(\psi(x)^*(\hat{p}/m)\psi(x))$$

- Now suppose this particle stream encounters a barrier:

$$U(x) = \begin{cases} 0 & \text{if } x < 0 \\ U_0 & \text{if } x > 0 \end{cases}$$

Assume for the moment that $E < U_0$ so that this is a true barrier. Solving the Schrodinger Equation yields the following solution

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & \text{if } x < 0 \\ Ce^{-\kappa' x} & \text{if } x > 0 \end{cases}$$

$$k = \sqrt{2mE/\hbar^2} \qquad \kappa' = \sqrt{2m(U_0 - E)/\hbar^2}$$

- Imposing continuity of ψ and $d\psi/dx$ at $x = 0$ yields

$$A + B = C \qquad ik(A - B) = -\kappa' C$$

which can be solved most easily for A and B in terms of C:

$$A = \frac{1}{2}\left(1 + \frac{i\kappa'}{k}\right) C \qquad B = \frac{1}{2}\left(1 - \frac{i\kappa'}{k}\right) C$$

The magnitudes are related by

$$|A| = |B| = \sqrt{1 + \frac{\kappa'^2}{k^2}}\,|C|$$

The ratio B/A is a pure phase

$$B/A = \frac{k - i\kappa'}{k + i\kappa'} = e^{-2i\phi}$$

where $\phi = \arctan(\kappa'/k)$.

- This solution represents an incident stream Ae^{ikx} coming in from $-\infty$ and travelling in the $+x$ direction, a reflected stream Be^{-ikx} travelling back to $-\infty$ in the $-x$ direction, and the penetration stream $Ce^{-\kappa' x}$ which has penetrated the forbidden region, and is in the process of being turned back. The currents associated with each of these streams are

$$\begin{aligned} J_{\text{inc}} &= |A|^2 \hbar k/m \\ J_{\text{refl}} &= |B|^2 \hbar(-k)/m = -J_{\text{inc}} \\ J_{\text{pen}} &= \Re(\psi_C^*(\hat{p}/m)\psi_C) \\ &= \Re\left(C^* e^{-\kappa' x} \frac{\hbar}{mi} \frac{d}{dx} C e^{-\kappa' x}\right) \\ &= \Re\left(-\frac{|C|^2 \hbar \kappa'}{mi} e^{-2\kappa' x}\right) \\ &= 0 \end{aligned}$$

  This makes sense: the particle rate of reflection should equal the particle rate of incidence since every particle gets reflected. The net current inside the forbidden region is zero because every particle that enters the forbidden region leaves it the same way it came in, through $x = 0$. There is no net transmission of particles to $+\infty$.

- In the limit $U_0 \to \infty$, $\kappa' \to \infty$ and $|C| \to 0$. The penetration distance $1/(2\kappa')$ also goes to zero and so particles do not penetrate into the forbidden region. The ratio $B/A \to -1$, and so the wave function becomes

$$\psi(x) = \begin{cases} A' \sin(kx) & \text{if } x < 0 \\ 0 & \text{if } x > 0 \end{cases}$$

  where $A' = 2iA$. This is the same solution that one should expect for any other wave that encounters a hard boundary in which a node is forced at the interface. Also note that this is essentially a particle in a box in the limit $L \to \infty$. In that limit, the set of allowed values of k becomes continuous.

- Now suppose that the particle stream encounters a step which is *not* a true barrier:

$$U(x) = \begin{cases} 0 & \text{if } x < 0 \\ U_0 & \text{if } x > 0 \end{cases}$$

but this time $E > U_0$. In fact, it may be the case that $U_0 < 0$. Solving the Schrodinger Equation in this case yields

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & \text{if } x < 0 \\ Ce^{ik'x} & \text{if } x > 0 \end{cases}$$

$$k = \sqrt{2mE/\hbar^2} \qquad k' = \sqrt{2m(E-U_0)/\hbar^2}$$

This solution represents an incident stream Ae^{ikx} coming from $-\infty$, a reflected stream Be^{-ikx} travelling back to $-\infty$, and a transmitted stream $Ce^{ik'x}$ continuing on to $+\infty$. The term $De^{-ik'x}$ is not included for $x > 0$ because we are not considering a situation where particles are streaming in from $+\infty$. If we want to cater to this possibility, we should add the term.

- Imposing continuity of ψ and $d\psi/dx$ at $x = 0$ yields

$$A + B = C \qquad ik(A - B) = ik'C$$

which can be solved for B and C in terms of A:

$$B = \frac{k-k'}{k+k'}A \qquad C = \frac{2k}{k+k'}A$$

- The currents associated with each stream are

$$\begin{aligned} J_{\text{inc}} &= \frac{\hbar k}{m}|A|^2 \\ J_{\text{refl}} &= \frac{\hbar(-k)}{m}|B|^2 = -\frac{\hbar k}{m}\frac{(k-k')^2}{(k+k')^2}|A|^2 = -\frac{(k-k')^2}{(k+k')^2}J_{\text{inc}} \\ J_{\text{tran}} &= \frac{\hbar k'}{m}|C|^2 = \frac{k'}{k}\frac{\hbar k}{m}\frac{4k^2}{(k+k')^2}|A|^2 = \frac{4kk'}{(k+k')^2}J_{\text{inc}} \end{aligned}$$

- The reflection and transmission coefficients are defined as follows:

$$R = \frac{|J_{\text{refl}}|}{|J_{\text{inc}}|} = \frac{(k-k')^2}{(k+k')^2}$$

$$T = \frac{|J_{\text{tran}}|}{|J_{\text{inc}}|} = \frac{4kk'}{(k+k')^2}$$

Note that $R + T = 1$, since the incident current should equal to the sum of the reflected and transmission current (taking all currents as positive

values). This will always happen. Note that these coefficients can also be defined for the step barrier that we considered earlier; in that case $R = |B|^2/|A|^2 = 1$ and $T = 0$ since there is no transmission through an infinitely long barrier.

- Now consider the finite barrier given by

$$U(x) = \begin{cases} 0 & \text{if } x < -L/2 \text{ or } x > L/2 \\ U_0 & \text{if } |x| < L/2 \end{cases}$$

where $U_0 > E$. Once again, we assume that an incident stream comes from $-\infty$ but that there is no stream coming in from $+\infty$. The general solution to the Schrodinger Equation with these assumptions can be written in the form

$$\psi(x) = \begin{cases} A_+ e^{ik(x+L/2)} + B_- e^{-ik(x+L/2)} & \text{if } x < -L/2 \\ C_+ e^{\kappa(x-L/2)} + C_- e^{-\kappa(x+L/2)} & \text{if } -L/2 < x < L/2 \\ B_+ e^{ik(x-L/2)} & \text{if } x > L/2 \end{cases}$$

$$k = \sqrt{\frac{2mE}{\hbar^2}} \qquad \kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$

The A_+ term represents the incident beam and B_- term represents the reflected beam. The $C_\pm$ terms represent penetration into the classically forbidden region. Since the barrier is finite, both in energy and length, it is possible for some of the incident particles to tunnel though to the other side. The B_+ term represents the transmitted stream.

- The coefficients $B_\pm$ and $C_\pm$ can be expressed in terms of A_+ by imposing the continuity conditions for ψ and $d\psi/dx$ at $x = \pm L/2$. The use of the balanced interval $[-L/2, L/2]$ and replacing x with $x \pm L/2$ in the exponents is done to facilitate this calculation, although the calculation is still very difficult. It can be done, however, and a derivation is given at the end of the lecture notes.

- The incident, reflected, and transmitted currents can be expressed in terms of these coefficients as follows:

$$\begin{aligned} J_{\text{inc}} &= \frac{\hbar k}{m}|A_+|^2 \\ J_{\text{refl}} &= -\frac{\hbar k}{m}|B_-|^2 \\ J_{\text{tran}} &= \frac{\hbar k}{m}|B_+|^2 \end{aligned}$$

It is also possible to evaluate the current inside the barrier region. The result is

$$J_{\text{bar}} = \frac{2\hbar\kappa}{m} e^{-\kappa L} \Im(C_-^* C_+)$$

which is independent of x and should equal J_{tran}. (Good HW problem: prove the above equation.)

- The reflection and transmission coefficients are given by

$$\begin{aligned} R &= |J_{\text{refl}}|/|J_{\text{inc}}| = |B_-|^2/|A_+|^2 \\ T &= |J_{\text{tran}}|/|J_{\text{inc}}| = |B_+|^2/|A_+|^2 \end{aligned}$$

  It should be possible with the full solution to show that $R + T = 1$.

- One of the most important quantities of interest is the tunnelling probability, which is given by the transmission coefficient. In the case where $\kappa L \gg 1$, $|B_+| \sim e^{-\kappa L}|A_+|$, and so

$$T \sim e^{-2\kappa L}$$

  This is actually a special case of a more general result known as the WKB approximation. This approximation applies to a long barrier described by a slowly varying potential energy function $U(x)$, and is given by

$$T \sim \exp\left(-2\int_a^b \kappa\, dx\right)$$

  where $[a, b]$ defines the interval over which $U(x) > E$ and

$$\kappa(x) = \sqrt{\frac{2m(U(x) - E)}{\hbar^2}}$$

- We have considered a number of situations involving an incident stream from $-\infty$ encountering forces near $x = 0$. In each such situation, we could have constructed a wave packet for the incident particle by combining Ae^{ikx} for different values of k.

$$\psi_{\text{inc}}(x) = \int_{-\infty}^{\infty} A(k) e^{ikx}\, dk$$

  The time development of the wave packet can be derived using the full time-dependent stationary state associated with each value of k:

$$\psi(x, t) = \int_{-\infty}^{\infty} \psi_k(x) e^{-i\omega_k t}\, dk$$

where

$$\psi_k(x) = \begin{cases} A(k)e^{ikx} + \dots & \text{incident/reflection region} \\ \dots & \text{barrier/transmission regions} \end{cases}$$

Note that $\psi_k(x)$ includes the incident, reflected, and transmitted streams, as well as penetration into forbidden regions, as appropriate. The coefficients associated with those streams are calculated from the incident coefficient $A(k)$ for each k separately. In this way, one can mathematically describe the particle as it encounters the step/barrier near $x = 0$. In this context, the reflection and transmission coefficients represent *probabilities* that the particle will reflect back to $-\infty$ vs. transmitting to $+\infty$.

Wave functions in three dimensions

- A particle in three dimensions is described quantum mechanically by a wave function $\psi(x, y, z, t)$. The probability of finding that particle in a rectangular region $[x, x + dx] \times [y, y + dy] \times [z, z + dz]$ at time t is

$$P(x, y, z, t)\, dx\, dy\, dz = |\psi(x, y, z, t)|^2\, dx\, dy\, dz$$

  This can also be written in vector form:

$$P(\vec{r}, t)\, d^3\vec{r} = |\psi(\vec{r}, t)|^2\, d^3\vec{r}$$

  where $d^3\vec{r}$ represents the volume of a small region in space.

- The probability of finding the particle in some region of space Ω can be obtained by integrating over the volume of that region:

$$P(\Omega) = \iiint_\Omega |\psi(\vec{r})|^2\, d^3\vec{r}$$

  If that region is rectangular (i.e., of the form $[x_i, x_f] \times [y_i, y_f] \times [z_i, z_f]$), then the integral can be done with cartesian coordinates:

$$P = \int_{x_i}^{x_f} dx \int_{y_i}^{y_f} dy \int_{z_i}^{z_f} dz\, |\psi(x, y, z)|^2$$

  The fact that the particle must be somewhere in space (with probability 1) leads to the following normalization condition:

$$\iiint_{\text{spc}} d^3\vec{r}\, |\psi(\vec{r})|^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\, |\psi(x, y, z)|^2 = 1$$

- A properly normalized wave function can be used to compute expectation values of $\vec{r}$, or any function thereof:

$$\langle f(\vec{r})\rangle = \iiint_{\text{spc}} d^3\vec{r}\, f(\vec{r})|\psi(\vec{r})|^2 = \iiint_{\text{spc}} d^3\vec{r}\, \psi(\vec{r})^* f(\vec{r})\psi(\vec{r})$$

  where the integrals are over the entire space.

- In three dimensions, the wave number k is replaced by a wave *vector* $\vec{k}$. A *plane wave* is a wave with a definite wave vector, and is given by

$$\psi_{\vec{k}}(\vec{r},t) = Ae^{i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}}t)}$$

  The wave fronts (where the exponential equals +1) are planes perpendicular to $\vec{k}$ and travel in the direction of $\vec{k}$ with a speed

$$v_p = |\vec{v}_p| = \frac{\omega}{|\vec{k}|}$$

- A wave packet can be formed by a superposition of plane waves:

$$\psi(\vec{r}) = \iiint_{\text{spc}} d^3\vec{k}\, A(\vec{k})e^{i\vec{k}\cdot\vec{r}}$$

  The amplitude function can be computed from $\psi(\vec{r})$ using the Fourier transform:

$$A(\vec{k}) = \frac{1}{(2\pi)^3}\iiint_{\text{spc}} d^3\vec{r}\,\psi(\vec{r})e^{-i\vec{k}\cdot\vec{r}}$$

  The full time dependence is given by

$$\psi(\vec{r},t) = \iiint_{\text{spc}} d^3\vec{k}\, A(\vec{k})e^{i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}}t)}$$

  and can be used to describe a particle travelling with the group velocity

$$\vec{v}_g = \frac{d\omega_{\vec{k}}}{d\vec{k}} = \vec{\nabla}_{\vec{k}}\,\omega_{\vec{k}}$$

- According to the de Broglie relation, plane waves $\psi_{\vec{k}}(\vec{r},t)$ are states with definite momentum

$$\vec{p} = \hbar\vec{k}$$

  The momentum operator is given by

$$\hat{\vec{p}} = \frac{\hbar}{i}\vec{\nabla}$$

and is now a vector operator. When applied to plane waves, the result is a definite value of momentum:

$$\hat{\vec{p}}\psi_{\vec{k}} = \frac{\hbar}{i}\vec{\nabla}\psi_{\vec{k}} = \frac{\hbar}{i}(i\vec{k})\psi_{\vec{k}} = \hbar\vec{k}\psi_{\vec{k}}$$

- The momentum operator can be used to compute expectation values of $\vec{p}$, or functions thereof:

$$\langle f(\vec{p})\rangle = \iiint_{\text{spc}} d^3\vec{r}\,\psi(\vec{r})^* f(\hat{\vec{p}})\psi(\vec{r})$$

The Schrodinger Equation in three dimensions

- The Hamiltonian operator for a particle moving in three dimensions and subject to conservative forces described by the potential energy function $U(\vec{r})$ is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})$$

The differential operator "∇^2" is the Laplacian, and is given (in cartesian coordinates) by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- The time-independent Schrodinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$$

can be used to find the stationary states $\psi(\vec{r})$ associated with a given energy E. The full time-development of such states is given by

$$\psi(\vec{r},t) = \psi(\vec{r})e^{-i\omega t} \qquad \omega = E/\hbar$$

and is a solution of the full time-dependent Schrodinger Equation

$$\frac{d\psi}{dt} = -\frac{i}{\hbar}\hat{H}\psi$$

- For the free particle ($U(\vec{r}) = 0$), the time-independent Schrodinger Equation reduces to

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi(\vec{r})$$

The solutions of this differential equation are the plane waves

$$\psi_{\vec{k}}(\vec{r}) = Ae^{i\vec{k}\cdot\vec{r}} \qquad E = \frac{\hbar^2|\vec{k}|^2}{2m}$$

The full time-dependence is given by

$$\psi_{\vec{k}}(\vec{r},t) = Ae^{i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}}t)} \qquad \omega_{\vec{k}} = \frac{\hbar|\vec{k}|^2}{2m}$$

The phase velocity and group velocity are given, respectively, by

$$\vec{v}_p = \frac{\omega_{\vec{k}}}{|\vec{k}|}\frac{\vec{k}}{|\vec{k}|} = \frac{\hbar\vec{k}}{2m} \qquad \vec{v}_g = \frac{d\omega_{\vec{k}}}{d\vec{k}} = \frac{\hbar\vec{k}}{m}$$

- Now consider the particle confined to an $L_x \times L_y \times L_z$ rectangular box (infinite potential well). The potential energy function is given by

$$U(x,y,z) = \begin{cases} 0 & \text{if } 0 \le x \le L_x,\ 0 \le y \le L_y, \text{ and } 0 \le z \le L_z \\ \infty & \text{otherwise} \end{cases}$$

The wave function outside of the box is identically zero, as before. The wave function inside the box is given by linear combinations of plane wave solutions with $\vec{k} = (\pm k_x, \pm k_y, \pm k_z)$ (8 terms). The plane waves themselves can be written

$$\psi(x,y,z) = Ae^{i(\pm k_x x \pm k_y y \pm k_z z)} = Ae^{\pm ik_x x}e^{\pm ik_y y}e^{\pm ik_z z}$$

The wave function can also be written as a linear combination of products of sines and cosines

$$\begin{aligned} \psi(x,y,z) \;=\; & B\sin(k_x x)\sin(k_y y)\sin(k_z z) \\ & + C\sin(k_x x)\sin(k_y y)\cos(k_z z) \\ & + D\sin(k_x x)\cos(k_y y)\sin(k_z z) + \ldots \qquad (8 \text{ terms}) \end{aligned}$$

- The wave function should be continuous at the boundary surface, which means that $\psi(x,y,z) = 0$ for all x, y, and z such that either $x = 0$ *or* $x = L_x$ *or* $y = 0$ *or* $y = L_y$ *or* $z = 0$ *or* $z = L_z$. This requires that *each* factor in each term must separately vanish at both 0 and the appropriate value of L (L_x, L_y, or L_z, as the case may be).

- The boundary conditions at zero lead to rejection of all terms except the first term:

$$\psi(x, y, z) = B \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

The boundary conditions at L_x, L_y, and L_z lead to

$$k_x L_x = n_x \pi \qquad k_y L_y = n_y \pi \qquad k_z L_z = n_z \pi$$

which restricts the allowed values of $\vec{k}$ to

$$\vec{k} = (\frac{\pi n_x}{L_x}, \frac{\pi n_y}{L_y}, \frac{\pi n_z}{L_z})$$

The result is a standing wave in three dimensions where the length of the box in each direction is an integer number of half-wavelengths in that direction. The energy of this stationary state is given by

$$E_{(n_x,n_y,n_z)} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

- For a cubic box ($L = L_x = L_y = L_z$), the allowed values of $\vec{k}$ become

$$\vec{k} = \frac{\pi}{L}(n_x, n_y, n_z)$$

and the energy becomes

$$E_{(n_x,n_y,n_z)} = \frac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

Note that some energy values have more than one possible value set of quantum numbers (n_x, n_y, n_z), and therefore, more than one possible state. This is referred to as *degeneracy*.

- Now let's consider the three-dimensional harmonic oscillator. The potential energy function is given by

$$U(x, y, z) = \tfrac{1}{2} k r^2 = \tfrac{1}{2} k x^2 + \tfrac{1}{2} k y^2 + \tfrac{1}{2} k z^2$$

- This potential energy function is an example of a *separable* potential energy function, in the sense that $U(x, y, z)$ can be written as a sum of separate functions of x, y, and z:

$$U(x, y, z) = U_x(x) + U_y(y) + U_z(z)$$

If we consider wave functions of the form

$$\psi(x,y,z) = \psi_x(x)\psi_y(y)\psi_z(z)$$

and plug that into the time-independent Schrodinger Equation, we get

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)(\psi_x(x)\psi_y(y)\psi_z(z))$$
$$+(U_x(x)+U_y(y)+U_z(z))\psi_x(x)\psi_y(y)\psi_z(z) = E\psi_x(x)\psi_y(y)\psi_z(z)$$

Splitting each term on the left-hand side of the equation into three terms, and then dividing out $\psi_x(x)\psi_y(y)\psi_z(z)$ yields

$$\left(-\frac{\hbar^2}{2m}\frac{\psi_x''(x)}{\psi_x(x)}+U_x(x)\right)+\left(-\frac{\hbar^2}{2m}\frac{\psi_y''(y)}{\psi_y(y)}+U_y(y)\right)$$
$$+\left(-\frac{\hbar^2}{2m}\frac{\psi_z''(z)}{\psi_z(z)}+U_z(z)\right)=E$$

- The above equation is in the form of

$$f(x)+g(y)+h(z)=C$$

This type of algebraic functional equation has a very important solution: *all three functions must be constant.* To see why, let x_1 and x_2 be given and choose y and z arbitrarily. Then

$$f(x_1) = C - g(y) - h(z) = f(x_2)$$

The proof that $g(y)$ and $h(z)$ are constant is similar.

- It follows that

$$-\frac{\hbar^2}{2m}\frac{\psi_x''(x)}{\psi_x(x)}+U_x(x)=E_x$$

which can be rewritten

$$-\frac{\hbar^2}{2m}\psi_x''(x)+U_x(x)\psi_x(x)=E_x\psi_x(x)$$

In a similar manner, we find

$$-\frac{\hbar^2}{2m}\psi_y''(y)+U_y(y)\psi_y(y)=E_y\psi_y(y)$$

$$-\frac{\hbar^2}{2m}\psi_z''(z) + U_z(z)\psi_z(z) = E_z\psi_z(z)$$

Plugging this back into the original time-independent Schrodinger Equation yields

$$E_x + E_y + E_z = E$$

- Evidently, the wave functions $\psi_x(x)$, $\psi_y(y)$, and $\psi_z(z)$ are stationary states of the one-dimensional Schrodinger Equation with potential energy functions $U_x(x)$, $U_y(y)$, and $U_z(z)$, respectively. The value of energy for the three-dimensional state is the sum of the energy values for the three constituent one-dimensional states. It also follows that if $\psi_x(x)$, $\psi_y(y)$, and $\psi_z(z)$ are properly normalized, then the product wave function is also normalized:

$$\begin{aligned}\iiint_{\text{spc}} d^3\vec{r}\,|\psi(x,y,z)|^2 &= \int_{-\infty}^{\infty} dx\,|\psi_x(x)|^2 \int_{-\infty}^{\infty} dy\,|\psi_y(y)|^2 \int_{-\infty}^{\infty} dz\,|\psi_z(z)|^2 \\ &= (1)(1)(1) = 1\end{aligned}$$

- We can apply this result to the harmonic oscillator. The constituent potential energy functions $U_x(x)$, $U_y(y)$, and $U_z(z)$ all describe harmonic oscillators with the same value of m and $\omega_0 = \sqrt{k/m}$. The corresponding stationary states are labeled with quantum numbers n_x, n_y, and n_z, and are given by

$$\begin{aligned}\psi_{x,n_x}(x) &= Af_{n_x}(x/a_0)e^{-x^2/4a_0^2} \qquad & E_x &= \hbar\omega_0(n_x + \tfrac{1}{2}) \\ \psi_{y,n_y}(y) &= Af_{n_y}(y/a_0)e^{-y^2/4a_0^2} \qquad & E_y &= \hbar\omega_0(n_y + \tfrac{1}{2}) \\ \psi_{z,n_z}(z) &= Af_{n_z}(z/a_0)e^{-z^2/4a_0^2} \qquad & E_z &= \hbar\omega_0(n_z + \tfrac{1}{2})\end{aligned}$$

  where $A = (2\pi)^{-1/4}a_0^{-1/2}$ is an overall normalization constant and $f_n(\eta)$ are the polynomial functions used in the solution to the one-dimensional harmonic oscillator.

- Putting this together yields the stationary states for the three-dimensional harmonic oscillator:

$$\psi_{(n_x,n_y,n_z)}(x,y,z) = A^3 f_{n_x}(x/a_0)f_{n_y}(y/a_0)f_{n_z}(z/a_0)e^{-r^2/4a_0^2}$$

  with energy

$$E_{(n_x,n_y,n_z)} = E_{n_x} + E_{n_y} + E_{n_z} = \hbar\omega_0(n_x + n_y + n_z + \tfrac{3}{2})$$

These states are characterized by the three quantum numbers (n_x, n_y, n_z) that characterize the constituent stationary states for the one-dimensional harmonic oscillator.

- These principles can also be applied to the particle in a box and the free particle, since both of those potential energy functions are separable. Note that the particle in the box solutions are products of solutions to the corresponding one-dimensional boxes, and that the allowed energies are sums of the corresponding energies for the one-dimensional boxes. It should be evident from our normalization discussion that the overall normalization factor for the particle in a box state should be $\sqrt{8/(L_x L_y L_z)}$. Also, note that the plane wave solutions for the free particle can be written

$$\psi_{\vec{k}}(x, y, z) = Ae^{ik_x x} e^{ik_y y} e^{ik_z z}$$

and that the energy of that state is given by

$$E_{\vec{k}} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$

- WARNING: The three-dimensional finite well potential defined by

$$U(x, y, z) = \begin{cases} 0 & \text{if } 0 \leq x \leq L_x,\ 0 \leq y \leq L_y, \text{ and } 0 \leq z \leq L_z \\ U_0 & \text{otherwise} \end{cases}$$

is *not* separable. In principle, this problem can be solved, but it is unlikely that the wave functions will be in the form of a product such as

$$\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z)$$

I'm not sure that the solution is easy to come by.

- This complication introduced by the finite well can be fixed if we are willing to modify the potential energy function as follows:

$$U(x, y, z) = \begin{cases} 0 & \text{if } 0 \leq x \leq L_x,\ 0 \leq y \leq L_y, \text{ and } 0 \leq z \leq L_z \\ U_0 & \text{if one coordinate } (x, \text{ } y, \text{ or } z) \text{ is out of range} \\ 2U_0 & \text{if two coordinates are out of range} \\ 3U_0 & \text{if all three coordinates are out of range} \end{cases}$$

This potential energy function *is* separable, and can be solved with products of solutions to the one-dimensional finite potential well.

Appendix: proof of $J = \Re(\psi^*(\hat{p}/m)\psi)$

- This result is essentially proved by demonstrating that the equation of continuity
$$\frac{d\rho}{dt} = -\frac{dJ}{dx}$$
is satisfied with $\rho = |\psi|^2$ and J as defined above. If the true current is J', then
$$\frac{d(J - J')}{dx} = \frac{dJ}{dx} - \frac{dJ'}{dx} = -\frac{d\rho}{dt} + \frac{d\rho}{dt} = 0$$
so that $J' - J$ is a position-independent (but possibly time-dependent) constant. The fact that the definition of J gives the physically correct value of current in the special case of a definite momentum state $\psi(x) = Ae^{ikx}$ is strong indication that $J' - J = 0$, and that J as defined above represents the true current in *all* situations, not just the special case of a definite momentum state. This is normally accepted as a satisfactory proof.

- Let's start by expressing J in terms of derivatives (let $\psi' = d\psi/dx$):
$$\begin{aligned} J &= \Re\left(\psi^* \frac{\hat{p}}{m}\psi\right) = \Re\left(\psi^* \frac{\hbar}{mi}\psi'\right) \\ &= \frac{\hbar}{2m}\left(\psi^* \frac{1}{i}\psi' + \psi \frac{1}{-i}\psi'^*\right) \\ &= \frac{\hbar}{2mi}(\psi^*\psi' - \psi'^*\psi) \end{aligned}$$
We used the fact that $\Re(z) = \frac{1}{2}(z + z^*)$.

- Now calculate dJ/dx:
$$\begin{aligned} \frac{dJ}{dx} &= \frac{\hbar}{2mi}(\psi'^*\psi' + \psi^*\psi'' - \psi''^*\psi - \psi'^*\psi') \\ &= \frac{\hbar}{2mi}(\psi^*\psi'' - \psi''^*\psi) \end{aligned}$$

- Now recall the time-dependent Schrodinger equation:
$$\frac{d\psi}{dt} = -\frac{i}{\hbar}\hat{H}\psi = -\frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\psi'' + U\psi\right)$$

The complex conjugate of this time derivative is given by

$$\frac{d\psi^*}{dt} = +\frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\psi''^* + U\psi^*\right)$$

- Now calculate the time derivative of $\rho = \psi^*\psi$:

$$\begin{aligned}
\frac{d\rho}{dt} &= \frac{d\psi^*}{dt}\psi + \frac{d\psi}{dt}\psi^* \\
&= \frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\psi''^*\psi + U\psi^*\psi + \frac{\hbar^2}{2m}\psi''\psi^* - U\psi\psi^*\right) \\
&= \frac{i}{\hbar}\frac{\hbar^2}{2m}\left(\psi''\psi^* - \psi''^*\psi\right) \\
&= -\frac{\hbar}{2mi}(\psi^*\psi'' - \psi''^*\psi) \\
&= -\frac{dJ}{dx}
\end{aligned}$$

Appendix: Finite barrier coefficients derivation

- Consider the finite barrier potential energy function:

$$U(x) = \begin{cases} 0 & \text{if } |x| < L/2 \\ U_0 & \text{if } |x| > L/2 \end{cases}$$

Solving the Schrodinger Equation yields the following general solution (assuming $E < U_0$):

$$\psi(x) = \begin{cases} A_+e^{ik(x+L/2)} + B_-e^{-ik(x+L/2)} & \text{if } x < -L/2 \\ C_+e^{\kappa(x-L/2)} + C_-e^{-\kappa(x+L/2)} & \text{if } -L/2 < x < L/2 \\ B_+e^{ik(x-L/2)} + A_-e^{-ik(x-L/2)} & \text{if } x > L/2 \end{cases}$$

$$k = \sqrt{\frac{2mE}{\hbar^2}} \qquad \kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$

- Three comments:
  - Once again, we use a balanced interval $[-L/2, L/2]$ in order to facilitate symmetry arguments.

- We replaced x by $x \pm L/2$ in the exponents to simplify the boundary conditions. Most of the exponents will be zero at the boundary points. The net result is an additive shift in the exponent, which results in multiplication of these terms by an overall constant. They affect the value of the coefficients, but not the fact that these functions are solutions to the time-independent Schrodinger Equation, nor the physical meaning behind each term.
- The term $A_- e^{-ik(x-L/2)}$, which describes an incoming stream of particles from $+\infty$, is included. Ultimately, we will set it to zero, but we include it initially to allow us to exploit symmetry.

- Some definitions that will come in handy later:

$$\mu = 1 + i\kappa/k = |\mu|e^{i\phi} \qquad \mu^* = 1 - i\kappa/k = |\mu|e^{-i\phi}$$
$$|\mu| = \sqrt{1 + \kappa^2/k^2} \qquad \phi = \arctan(\kappa/k)$$
$$r = e^{-\kappa L} \qquad \gamma_\pm = 1 \pm e^{-2i\phi} r$$

  Thus,

$$\mu \pm \mu^* r = |\mu| e^{i\phi} \gamma_\pm \qquad \mu^* \pm \mu r = |\mu| e^{-i\phi} \gamma_\pm^*$$

- Boundary conditions at $x = L/2$:

$$\psi(L/2) = C_+ + C_- r = B_+ + A_-$$
$$\psi'(L/2) = \kappa(C_+ - C_- r) = ik(B_+ - A_-)$$

  Rewriting the second equation

$$(-i\kappa/k)(C_+ - C_- r) = B_+ - A_-$$

  First adding and then subtracting this equation from the first one yields B_+ and A_- in terms of $C_\pm$:

$$B_+ = \tfrac{1}{2}(\mu^* C_+ + \mu C_- r) \qquad A_- = \tfrac{1}{2}(\mu C_+ + \mu^* C_- r)$$

  Boundary conditions at $x = -L/2$ will be taken care of using symmetry.

- Even functions: $\psi_e(-x) = \psi_e(x)$.

$$A_+ = A_- = A_e \qquad B_+ = B_- = B_e \qquad C_+ = C_- = C_e$$

  Therefore,

$$B_e = \tfrac{1}{2} C_e(\mu^* + \mu r) = \tfrac{1}{2}|\mu| e^{-i\phi} \gamma_+^* C_e$$
$$A_e = \tfrac{1}{2} C_e(\mu + \mu^* r) = \tfrac{1}{2}|\mu| e^{i\phi} \gamma_+ C_e$$

- Odd functions: $\psi_o(-x) = -\psi_o(x)$.

$$A_+ = -A_- = A_o \qquad B_+ = -B_- = B_o \qquad C_+ = -C_- = C_o$$

Therefore,

$$B_o = \tfrac{1}{2}C_o(\mu^* - \mu r) = \tfrac{1}{2}|\mu|e^{-i\phi}\gamma_-^* C_o$$
$$A_o = -\tfrac{1}{2}C_o(\mu - \mu^* r) = -\tfrac{1}{2}|\mu|e^{i\phi}\gamma_- C_o$$

- General function: $\psi(x) = \psi_e(x) + \psi_o(x)$.

$$A_\pm = A_e \pm A_o \qquad B_\pm = B_e \pm B_o \qquad C_\pm = C_e \pm C_o$$

- *Now* set $A_- = 0$. Then $A_e = A_o$, and so

$$A_+ = A_e + A_o = 2A_e = 2A_o$$

- Solve for $B_\pm$ and $C_\pm$ in terms of A_+.

$$\begin{aligned}
C_e &= \frac{2A_e}{|\mu|e^{i\phi}\gamma_+} = \frac{e^{-i\phi}}{|\mu|\gamma_+}A_+ \\
C_o &= -\frac{2A_o}{|\mu|e^{i\phi}\gamma_-} = -\frac{e^{-i\phi}}{|\mu|\gamma_-}A_+ \\
B_e &= \frac{1}{2}|\mu|e^{-i\phi}\gamma_+^*\left(\frac{e^{-i\phi}}{|\mu|\gamma_+}A_+\right) = \frac{1}{2}e^{-2i\phi}\frac{\gamma_+^*}{\gamma_+}A_+ \\
B_o &= \frac{1}{2}|\mu|e^{-i\phi}\gamma_-^*\left(-\frac{e^{-i\phi}}{|\mu|\gamma_-}A_+\right) = -\frac{1}{2}e^{-2i\phi}\frac{\gamma_-^*}{\gamma_-}A_+
\end{aligned}$$

and so

$$\begin{aligned}
B_\pm &= B_e \pm B_o = \frac{1}{2}e^{-2i\phi}\left(\frac{\gamma_+^*}{\gamma_+} \mp \frac{\gamma_-^*}{\gamma_-}\right)A_+ \\
C_\pm &= C_e \pm C_o = \frac{e^{-i\phi}}{|\mu|}\left(\frac{1}{\gamma_+} \mp \frac{1}{\gamma_-}\right)A_+
\end{aligned}$$

- Some math involving $\gamma_\pm$:

$$\begin{aligned}
\gamma_+\gamma_- &= (1 + e^{-2i\phi}r)(1 - e^{-2i\phi}r) = 1 - e^{-4i\phi}r^2 \\
\gamma_+^*\gamma_- &= (1 + e^{2i\phi}r)(1 - e^{-2i\phi}r) = \underbrace{(1 - r^2)}_{\text{real}} + \underbrace{(e^{2i\phi} - e^{-2i\phi})r}_{\text{imaginary}} \\
\gamma_+ + \gamma_- &= 2 \\
\gamma_+ - \gamma_- &= 2e^{-2i\phi}r \\
\gamma_+^*\gamma_- + \gamma_+\gamma_-^* &= 2(1 - r^2) \\
\gamma_+^*\gamma_- - \gamma_+\gamma_-^* &= 2(e^{2i\phi} - e^{-2i\phi})r
\end{aligned}$$

- Complete the calculation of $B_\pm$ and $C_\pm$:

$$\begin{aligned}
B_+ &= \frac{1}{2}e^{-2i\phi}\left(\frac{\gamma_+^*\gamma_- - \gamma_+\gamma_-^*}{\gamma_+\gamma_-}\right)A_+ \\
&= e^{-2i\phi}\frac{(e^{2i\phi}-e^{-2i\phi})r}{1-e^{-4i\phi}r^2}A_+ \\
&= \frac{(1-e^{-4i\phi})e^{-\kappa L}}{1-e^{-4i\phi}e^{-2\kappa L}}A_+ \\
B_- &= \frac{1}{2}e^{-2i\phi}\left(\frac{\gamma_+^*\gamma_- + \gamma_+\gamma_-^*}{\gamma_+\gamma_-}\right)A_+ \\
&= e^{-2i\phi}\frac{1-r^2}{1-e^{-4i\phi}r^2}A_+ \\
&= e^{-2i\phi}\frac{1-e^{-2\kappa L}}{1-e^{-4i\phi}e^{-2\kappa L}}A_+ \\
C_+ &= -\frac{e^{-i\phi}}{|\mu|}\left(\frac{\gamma_+ - \gamma_-}{\gamma_+\gamma_-}\right)A_+ \\
&= -\frac{e^{-i\phi}}{|\mu|}\,\frac{2e^{-2i\phi}r}{1-e^{-4i\phi}r^2}A_+ \\
&= -\frac{2e^{-3i\phi}}{|\mu|}\,\frac{e^{-\kappa L}}{1-e^{-4i\phi}e^{-2\kappa L}}A_+ \\
C_- &= \frac{e^{-i\phi}}{|\mu|}\left(\frac{\gamma_+ + \gamma_-}{\gamma_+\gamma_-}\right)A_+ \\
&= \frac{e^{-i\phi}}{|\mu|}\frac{2}{1-e^{-4i\phi}r^2}A_+ \\
&= \frac{2e^{-i\phi}}{|\mu|}\frac{1}{1-e^{-4i\phi}e^{-2\kappa L}}A_+
\end{aligned}$$